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CURRENT TECHNOLOGY IN OIL ANALYSIS SPECTROMETERS AND WHAT WE MAY EXPECT IN THE FUTURE

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Abstract: Oil analysis spectrometers have been in use for the analysis of wear metals, contaminants and additives in lubricating oils for almost 50 years. They have become the mainstay and primary analytical tool of most machine condition monitoring programs based on oil analysis. Spectrometers have evolved from large instruments that take up the better part of a laboratory, to smaller table top instruments. Analysis times have decreased from hours to seconds, and the instruments no longer have to be operated by experts to obtain excellent analytical results

This paper traces the history of the atomic spectroscopy technique through current instrumentation and capabilities. It will close with recent advances in technologies that have created remarkable opportunities to develop a new generation of oil analysis spectrometers

Key Words: Atomic absorption; Atomic emission; Inductively coupled plasma; Machine condition monitoring; Oil analysis; Rotating disc electrode; Spectrometers

HISTORY OF SPECTROSCOPY: Principles of spectroscopy go back close to four hundred years. However, modern spectroscopy has its origin in the early nineteenth century.

As with many of today's technological advances, spectroscopy can also trace some of its early days to Newton. While carrying out tests in 1666 with a glass prism, Newton noticed that sunlight is divided into spectral colors (rainbow colors), Figure 1. This basic fact of science is still the operational basis of all modern spectrometers.

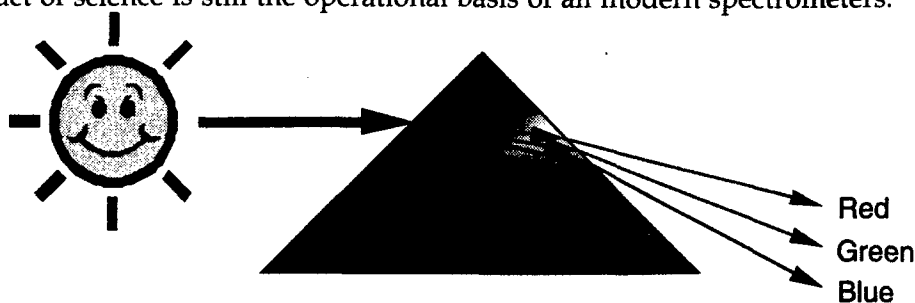


Figure 1, Newton's Experiment with Sunlight and a Prism

The nineteenth century started with further experimentation that eventually resulted in simple spectrographic instruments. In 1802 Wollaston found dark lines in the spectrum of the sun when he used an entrance slit as an aperture [1]. Fifteen years later, Fraunhofer produced the first diffraction grating and constructed a simple spectroscope to study the dark lines indicated by Wollaston. He found 700 of these lines in the spectrum of the sun and similar lines in the stars. In 1826 Talbot and Herschel introduced sodium, potassium, lithium and strontium salts into a spirit flame and observed the colors emitted by means of a spectroscope. The emission lines lay where Fraunhofer found the dark lines in the spectra of the sun and stars. Talbot recommended that this method be used to determine the presence of specific substances instead of an expensive chemical analysis.

In 1860 Bunsen and Kirchhoff extended the observations made by Talbot and Herschel. They recognized that spectral lines were connected with the atoms and not with their chemical compounds. The various atoms emit spectral lines that are unique to the elements excited in the flame. Emissions of these unique spectral lines can thus be used as evidence for the presence of these elements in the sample. This in essence, was the foundation stone for spectrochemical analysis. Kirchhoff also postulated on emission and absorption by stating that matter absorbs radiation at the same wavelength that it emits radiation. It was thus possible to explain the Fraunhofer lines in the spectrum of the sun as due to absorption by atoms in the cooler outer zones of the radiating source.

In 1869 Ångström produced the first reflection grating by scratching a mirror with a diamond to create parallel lines. Sample introduction was the area of study for Gouy and less than ten years later, he introduced the first pneumatic nebulizer to introduce liquids into flames.

At this time spectroscopy was a qualitative analytical technique. Spectra were initially observed visually using a spectroscope, but soon thereafter, they were photographed. Around the turn of the century, in the early 1900's, the spectroscope became a spectrograph when photographic plates were fitted to the image plane of the optics. It was also determined that few spectral lines lie in the visual part of the spectrum, and the majority are located in the ultra-violet region. Gas filled optical systems were thus developed to observe spectra below 190 nanometers which otherwise would be absorbed by air (oxygen).

In the 1930's emphasis shifted to alternative excitation sources because flame temperatures are too low to vaporize and excite most lines. Direct current (DC) arcs, alternating current arcs (AC), interrupted arcs and high voltage sparks were developed because they vaporize all elements and excite several spectral lines for each.

Modern spectroscopy was born in 1936 when Thanheiser and Heyes reported the first photoelectric detection of a spectrum using photocells. A few years later, the

development of photomultiplier tubes let to the introduction of today's modern "direct-reading spectrometers". Rotating disc electrode (RDE) systems replaced many flames as the preferred means to introduce the sample into an arc or spark for excitation. The main building blocks of spectrochemical analysis instruments became the excitation source, optical system (spectrometer), and readout system.

Since that time advances have been made in grating production, excitation sources and computerization. Gratings were expensive to produce and each was individually manufactured. When it was learned to copy gratings using a photographic replication process, they became less expensive to produce and prisms were eliminated from most spectrometers.

From 1965 to 1970 Greenfield and Fassel developed the inductively coupled plasma (ICP) source which exhibits much improved capabilities to excite spectral lines, and without most spectral interferences. This led to a renaissance for spectrochemical analysis and the ICP is still the most important excitation source for environmental analysis and research applications.

Starting with the late 1960's, computers started to be used to convert spectrometric measurements into actual concentrations. Analysis times were shortened, but most importantly, the human element was eliminated from much of the analysis process.

In 1983 fiber optics were introduced to transmit light from the excitation source to the spectrometer optics. This eliminated the need for complex optics and made it possible to manufacture stable and modular instruments. Until this time, spectrometer systems were restricted to laboratory use due to their need for environmental controls and complex operating requirements. The fiber optic which simplified construction, and computerization which simplified operation made it possible to develop mobile instruments. The entire industry changed, and it was possible for the first time to bring the instrument to the site where the analysis was required, rather than having to take the sample to a laboratory.

The Joint Oil Analysis Program is a direct beneficiary from these developments. Today oil analysis spectrometers are mobile, easier to use and more reliable.

TODAY'S SPECTROMETERS FOR OIL ANALYSIS: Spectrometers used for debris and lubricant analysis fall into two categories, atomic absorption and atomic emission. Atomic absorption spectrometers consist of flame instruments (FL/AAS) and atomic emission spectrometers can be either rotating disc electrode (RDE/AES) or inductively coupled plasma (ICP/AES). Each technique will be described briefly in this section.

Atomic Absorption Spectroscopy (AAS): In the flame atomic absorption spectroscopy (FL/AAS) technique, Figure 2, a small amount of diluted oil sample is fed into a controlled flame normally fueled by an acetylene-oxygen or nitrous oxide mixture. The flame vaporizes the sample and stimulates the atoms into an elevated energy

state so they can readily absorb light. A special hollow cathode lamp emits a high intensity light beam corresponding to the exact energy required to cause the element of interest to be raised to an excited energy state. Since the lamp emits light at the specific wavelength of the element to be analyzed, a separate lamp is required for each element. The monochromator is tuned to the desired wavelength and because of the chopper, receives a continuous reference signal from the hollow cathode lamp and an alternating absorbed signal from the flame. The absorbed light can be related to the concentration of the element present in the oil [2], and a microprocessor or computer then separates the signals and converts them into concentrations.

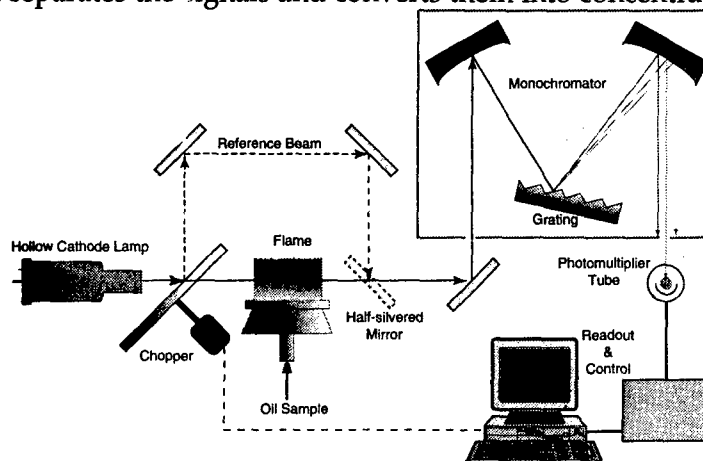


Figure 2, Schematic diagram of an atomic absorption spectrometer (AAS)

The FL/AAS technique has been in use for over 35 years in thousands of instruments for elemental analysis but is applied most often for aqueous solutions, rather than oil samples. It is a single element at a time technique that is good for quantitative, not qualitative, analysis. Improvements in the past 10 years have been in alternate means to atomize the sample [3].

The FL/AAS technique is relatively simple to operate, offers good analytical performance and is the least costly instrument to acquire. It is, however, relatively slow, involves sample preparation for most oils, and requires a different light source for each element analyzed. The sample introduction system and flame temperature limit the wear particle size detection capability to about 5 μm [4]. Table 1 summarizes advantages and disadvantages of the AAS technique.

Table 1, Advantages and Disadvantages of the AAS Technique

Advantages

- simple to operate
- analytical performance
- virtually free of spectral interferences
- low purchase price

Disadvantages

- slow, one element at a time
- sample preparation
- inefficient for particles > 5 μm
- requires gases & light sources

Analytical instruments using the AAS technique are considered ideal starter systems and are used in applications where few samples have to be analyzed at any one time.

Atomic Emission Spectroscopy (AES): Most atomic emission spectrometers employed in used oil analysis are either of the rotating disk electrode type (RDE) or of the inductively coupled plasma (ICP) type. In the RDE/AES technique, Figure 3, a rotating disc electrode brings a continuous sample into a gap between the disc and a stationary rod electrode. A high voltage arc is then struck between the disc and rod electrodes causing the individual atoms in the sample to give off light or radiant energy.

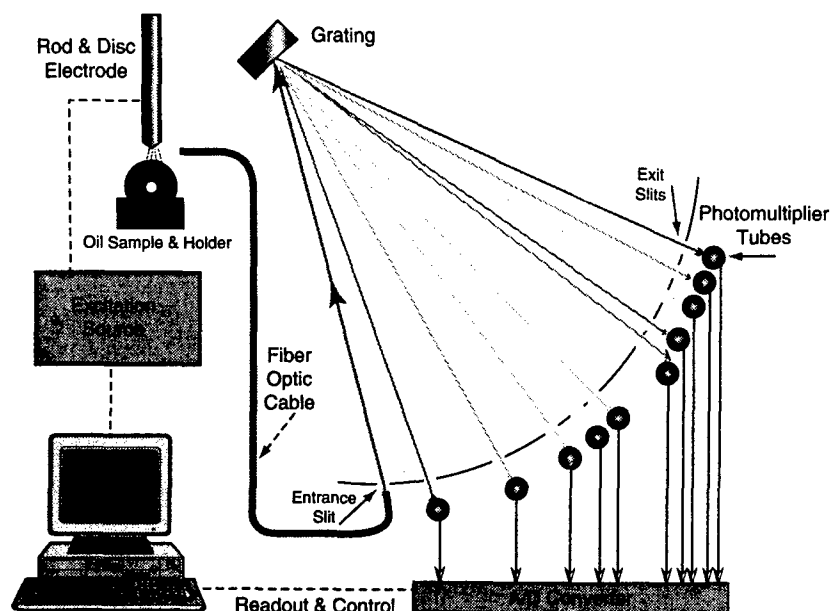


Figure 3, Schematic diagram of an RDE atomic emission spectrometer

The ICP/AES excitation technique employs an electrode-free plasma created by a flow of inert gas (argon). The gas passes continuously through the plasma torch which is located inside a two or three turn R.F. coil connected to a radio frequency alternating current generator, Figure 4. The argon gas acts as the secondary winding of a transformer, becoming highly ionized and extremely hot. The ionized argon is referred to as a plasma and reaches temperatures of 8,000 to 10,000°C. The oil sample is aspirated through the center of the torch and into the plasma where the atoms present are totally dissociated and excited sufficiently to give off radiant energy.

In RDE/AES and ICP/AES systems, a lens or fiber optic is then used to gather and focus the radiant energy from the excitation source onto a concave diffraction grating which disperses the light into the various spectral lines associated with the elements present. Photomultiplier tubes are positioned behind exit slits to detect and convert radiant energy into electrical currents which give a measure of the concentration of

each metal present in the sample. This result is displayed on a video screen, sent to a printer or stored on a hard disc. While the ICP technique was developed for water analysis, improvements have continued for various applications including oil analysis.

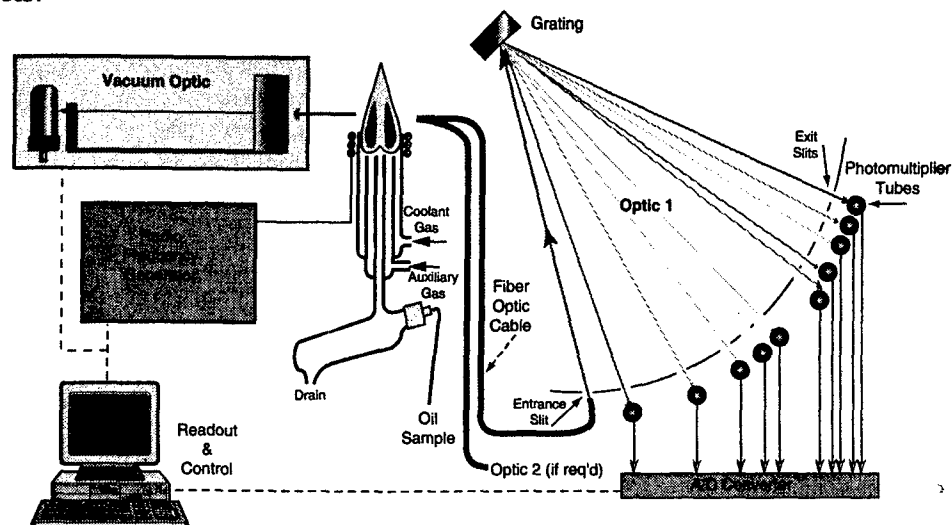


Figure 4, Schematic diagram of an ICP atomic emission spectrometer

For lubricating oil and fuel analysis, the RDE technique continues to be preferred for its simplicity of operation and reliability. It also has the ability to more efficiently analyze the larger particulates in used oil samples ranging from light distillate fuels to heavy gear oils and even greases which can be analyzed without dilution. The technique is very robust, has few moving parts and requires little maintenance. It has been the only viable choice for field deployable spectrometers for commercial and military applications. Table 2 summarizes the advantages and disadvantages of the RDE Technique.

Table 2, Advantages and Disadvantages of the RDE Technique

| <u>Advantages</u> | <u>Disadvantages</u> |
|---|---|
| <ul style="list-style-type: none"> • simple to operate • no sample preparation • robustness • does not require cooling water or gases • little maintenance | <ul style="list-style-type: none"> • matrix effect • only oil based samples • inefficient for particles $>10\mu\text{m}$ |

The advantages and disadvantages of the ICP technique are summarized in Table 3. The main advantage of the ICP technique is its performance: accuracy, precision and detection limits are excellent. Matrix effects are minimal since samples must be diluted prior to analysis and the diluent becomes the primary base material. The ICP also lends itself to analysis of almost any material that can be dissolvable so that a fine spray is created prior to analysis. Automation of the sample introduction process is widely practiced in some cases; unattended operation is thereby possible.

Table 3, Advantages and Disadvantages of the ICP Technique

| <u>Advantages</u> | <u>Disadvantages</u> |
|--|--|
| <ul style="list-style-type: none">• performance• limited matrix effect• flexibility (other materials)• automation | <ul style="list-style-type: none">• requires sample preparation• requires laboratory environment• inefficient for particles $>5\mu\text{m}$• requires gas (argon) |

The primary limitation of the ICP technique is the need to dilute an oil sample with a solvent prior to analysis. This time-consuming step can lead to accuracy errors. Operation of the ICP also requires a relatively well-trained person with experience in basic laboratory procedures. Used oil samples are not ideally suited for the sample introduction system, and a certain amount of care and cleaning is routinely required. It is not the kind of instrument one would place on the factory floor. The particle size analysis efficiency is worse than the RDE technique and limits its ability to detect certain types of severe wear conditions

TOMORROW'S SPECTROMETERS FOR OIL ANALYSIS: Atomic emission spectrometers have become the primary technique for used oil wear metal and contaminant analysis. Our discussion regarding future improvements will thus be limited to this technique. The most logical approach is to review each of the main assemblies of a spectrometer system and discuss possible changes we might see in the future.

Excitation Source: Both the RDE and ICP technique provides acceptable analytical performance for used oil analysis. Wear metals and contaminants are usually in the oil samples in parts per million (ppm) concentrations; lower detection limits are not necessary. Accuracy is also acceptable for used oils but could be improved for the RDE technique when applied to quality control of additives. Most improvements will thus be in the cost, size and serviceability of future excitation sources.

All excitation sources are based on simple electronic circuitry using discreet components. Development trends tend to be towards solid state excitation circuits which result in cost, size and serviceability improvements. One of the side benefits will be the elimination of transformers that are bulky and extremely heavy.

Sample introduction is still one of the weak links of the RDE and ICP spectrometers. Pre-digestion and complex sample preparation procedure to improve particle size analysis capabilities have not been acceptable. Particle size limitations will be improved with simple ancillary systems such as the rotrode filter spectroscopy RFS method. Automation for sample introduction will also be a primary area of improvement. Automatic samplers and dilutors already exist for ICP spectrometers and work relatively well with many types of oils. The RDE technique has been a little more difficult to automate. However, several methods are in development and will be commercially available in the near future.

One of the biggest limitations to excitation source improvement is the requirement for instruments to meet and correlate to the existing JOAP data base. The JOAP data base has become a standard in the military, is extremely well documented and accepted and used by numerous worldwide military organizations. It is, however, based on instrument performance and referencing methods that are over thirty years old. Improvements that have been made to excitation sources often cannot be implemented if the instrument is to be used, and approved to analyze oil samples as an integral part of the JOAP.

Optical Systems: The optical systems of spectrometers have always been the primary factors in determining the size of an instrument. Improvements in gratings have made it possible to reduce size without sacrificing performance or dispersion. The early instruments with 3 meter (9 feet) focal curves were replaced with 2 meter, then 1 meter and today as small as 0.3 meter optics. Reduced requirements in focal curve size have made it possible to build much smaller instruments with better stability. The introduction of fiber optics has also led to further improvements in stability, complexity and size of optical systems.

The optical system is still the most expensive, the largest and the most delicate component of an instrument. However, rapidly developing solid-state detector technology in the form of charged coupled devices or CCD detectors may change all that. This technology provides devices, by a variety of processes, consisting of many small light sensitive semiconductors (pixels) which may be arranged in a single row (linear array) or as a rectangle or square (area array). CCD technology is widely applied in such commonplace and reliable devices as video cameras, copy and fax machines. Consequently, a robust industry exists to supply and improve such devices and they are available at favorable prices.

A linear array may be positioned at the focal surface of a spectrometer optic such that an entire emission spectrum may be measured pixel by pixel. Linear arrays are now commercially available having as many as 8000 pixels with pixel spacing of approximately 10 micrometers. Bearing in mind that in the present construction of a polychromator optic, exit slits placed in front of photomultiplier tubes are often 10 micrometers wide, never narrower and often wider, a CCD linear array can achieve the same selectivity as an exit slit, and does so for every location along the spectrum. This opens the possibility of simultaneous measurement everywhere along the emission spectrum which, in turn, means unlimited choice of elements within the spectral range of the optic. Further to freely choosing any element, two additional benefits now exist. Namely, simultaneous background correction is possible at any spectral position and an element may be measured at several emission wavelengths instead of one. These features are available in conventional polychromator optics, but only at substantial additional expense and without flexibility after construction, perhaps even compromising some wavelengths because of inevitable mechanical constraints.

By placing these miniaturized and high resolution linear arrays along the focal surface of spectrometer optics as described in the preceding paragraph, the possibility is created of designing a significantly smaller optic. Resolution may not be improved in all cases, but what exists may be adequate for routine oil analysis, especially if spectral interferences can be avoided by choosing analytical wavelengths with somewhat more freedom than photomultiplier tube detectors allow.

CCD technology has already been incorporated in several commercial ICP spectrometers, but not demonstrably with the cost/benefit that might ultimately derive. We should expect time to improve this situation.

At present, several problems hamper realization of full CCD potential.

1. Photometric sensitivity is not as good as with vacuum tube photomultipliers which have very low noise levels and excellent amplification.
2. CCD arrays require cooling (to -20 C and below) to improve noise reduction.
3. CCD semiconductors perform less well in the deep UV portion of the spectrum (which is probably not important for oil analysis - JOAP instruments operate at air path wavelengths, i.e., above 210 nm).
4. Fast computers and new software are required to interface the huge amounts of data generated by the many active pixels. However, the enormous increase in computing power that we have seen in the last few years has rendered it possible, even commonplace, to use analytical techniques that heretofore would have been considered impractical because of "number crunching" demands.

Readout Systems: The readout system of a spectrometer is used to control spectrometer operation and to collect the signals from the optics and to convert them to concentrations for the elements that have been detected in an oil sample. The readout system thus consists of hardware and software.

In the past, readout system hardware was complex and differed greatly among manufacturers. Today, except for one or two circuits, the personal computer is becoming more and more the only electronic readout system required for the spectrometer. It provides instrument control, data processing and troubleshooting. In the future, readout systems will become smaller and less expensive and in direct proportion with developments in the computer market.

The future will also bring improvements in software making instruments easier to operate, improving data bases, providing artificial intelligence and on-board instruction and maintenance manuals. Improvements in processing speed will be transparent as the integration time, up to 30 seconds, to collect the signal from the optics is still the limiting time factor.

As computerization was used more and more in spectrometers during the late 1980's, software was envisioned to be the panacea and solution to everything. Flato's quote [5] still applies today and most likely will apply in the future.

"Those of us who were there (speaking of the late 1980's) can well remember the mistaken belief that software was easier to develop than hardware, and would take less time. This misunderstanding led to endless 36-hour workdays, many missed shipping schedules, and just as many financial problems."

CONCLUSION: There will be changes in tomorrow's oil analysis spectrometer, but they may not be apparent to the operator of the instrument. Changes will be in the internal components of the instruments, there may be additional capabilities and applications, but performance will probably improve little. Since performance for oil analysis with today's spectrometers is more than acceptable, the main benefit derived by the user from instruments in the future will be:

- smaller size and weight
- more capabilities
- easier operation
- additional applications
- lower cost

Changes to solid state excitation sources and CCD technology in optical systems will reduce the size and weight of instruments by at least a factor of two. More capabilities will be possible with solid state detector based electronics and instruments will no longer be limited to only those elements installed when they were purchased. Every spectral line will be available to the user and can be selected with software that is easy to use and operate. The availability of more elements and fewer compromises in the construction of the optics will open additional applications for oil analysis spectrometers. Fuel and coolant analysis is already possible but performance will be improved. Lower cost of instruments will also make them available to other markets and potential user that could not afford these instruments before.

Spectrometers for oil analysis have evolved from instruments that had to be used in environmentally controlled laboratories and by expert and well trained scientific personnel. Today they have become easier to operate, smaller in size, mobile, and more robust for use in non laboratory environments. The net effect has been an analytical capability that provides information immediately and at the site where it is actually needed. The primary advantage of tomorrow's spectrometer will be in its expanded capabilities and lower cost. They will open up additional markets, but most important, the lower cost will make the technology available to users who until then were economically unable to benefit from machine condition monitoring based on oil analysis.

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